

EtO Ambient Air Sampling Procedures Using Canisters with Passive Vacuum Regulators

The procedure presented is designed for sampling volatile organic compounds (VOCs) in ambient air, based on the collection of whole air samples in SUMMA® treated canisters to final pressures below atmospheric. The samples are then analyzed using EPA Compendium Method TO-15 *Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*.

Sampler Installation

1. The sampling system consists of two components: a sample canister and a passive vacuum regulator (Veriflow vacuum regulator with gauge and sample inlet probe). The canisters have been cleaned, tested for contamination (blanked) and evacuated, the passive collection assemblies will have been cleaned, tested for contamination (blanked), and calibrated for 24-hour integrated sampling.
2. The complete sampling system must be securely mounted on a support structure which ensures that the sample inlet meets the siting criteria (See QAPP for details <https://www.epa.gov/il/quality-assurance-project-plan> section 2.1.2).
3. For collocated samplers, horizontal spacing should be between 0 and 4 meters, and inlet heights within 1 meter vertically.

OPERATING PROCEDURE

A. Equipment and Supplies

1. 6-liter sample collection canister
2. Veriflow vacuum regulator/gauge/inlet probe (passive collection assembly)
3. Chain of Custody (COC) form

B. Sampler and Sample Media Receipt Activities

Complete Sampling System

1. Check parts and components to ensure none is damaged.
2. Ensure all fittings are present and in good condition.
3. Prior to sampling keep all sampling system components in a clean area free of contamination.
4. Ensure the canister is not damaged. Confirm that the valve remained in the closed position during transport and that the top plug is secured on the bellows valve inlet fitting.

C. Preparing for a Sampling Event

1. Prepare sample paperwork. On the COC, supply all required information in the “Lab Pre-Sampling” section. Record any pertinent observations in the “Comments” section at the bottom of the form.
2. Remove the plug attached to the bellows valve inlet. Retain the plug in a clean place so that it can be used to reseal the bellows valve inlet after the sampling event.
3. Assemble the complete sampling system.
 - a. Attach the outlet fitting of the Veriflow vacuum controller to the canister bellows valve inlet fitting. *Note: Do not over tighten the fitting nut. When the fitting nut feels snug by*

hand, another quarter turn should be sufficient to secure the controller inlet to the canister.

- b. Ensure that the plug at the inlet of the Veriflow remains tight in order to perform a leak check. Perform a leak check by opening and then immediately closing the canister valve. Observe the vacuum reading on the Veriflow gauge. If the vacuum changes by more than 1 in Hg over 5 minutes, ensure that all fittings are tight. If all fittings are tight, then assemble another sampling system using another canister and repeat steps 2 and 3.

D. Sampling and Data Collection

1. Record the initial collection start time and date in "Setup Date:" in the "Field Setup" section on the COC form. Fully open the canister bellows valve. Observe the pressure (i.e., "Hg vacuum") indicated on the gauge.
2. After 24 hours, read the gauge and record the remaining pressure left in the can on the COC and record the reading in the "Field Recovery", "Field Final Can. Press. ("Hg)" blank. If the pressure is zero, note the lack of pressure in the "Comments" section of the form.
3. Close the canister bellows valve fully.
4. Disconnect the canister from Veriflow vacuum controller by unfastening the Veriflow outlet fitting from the canister bellows valve inlet fitting.
5. Replace and secure the retained plug on the canister bellows valve.
6. On the COC, supply all required information in the "Field Recovery" section. Be sure to record any observations that were made during the run period in the "Comments:" section.

Technical Note on Ethylene Oxide analysis by EPA TO-15 Method

Ethylene oxide (EtO) is an emerging pollutant that is quantified using the existing EPA TO-15¹ method with some modifications. The typical method setup scans for selected fragment ions (also known as selected ion monitoring mode or SIM) instead of a full spectrum scan in order to increase the analytical sensitivity and efficiency. However, SIM introduces uncertainties and limitations due to decreased collected full scan spectra information. Using SIM, another compound with common fragment ions (primary and secondary) and similar retention time windows as the target compound could be an interferant to the target compound, biasing quantitation results.

The EPA contract laboratory has confirmed that trans-2-butene co-elutes with EtO, creating an interference. The monitoring ions the contract laboratory selected for EtO before October 2018 were 15, 29 and 43; EtO was quantitated based on ion 29. Upon discovery of the interferant, the contract laboratory modified their analytical method to include additional unique confirmatory fragment ions to aid the identification and quantification processes. The modified method is scanning for ions 15, 29, 44, and 41 as well as ion unique to trans-2-butene (ion 56). For quantitation, the most intense ion 29 from EtO is used as the base quantitation peak (ions 15 and 44 as qualifying ions). Although the second most abundant ion (44) is in EtO and absent from trans-2-butene, the lower sensitivity and variable background issues (eg. carbon dioxide) associated with ion 44 make it less desirable for quantitation of EtO. The contract laboratory has analyzed standards that include EtO and the interferant trans-2-butene and is able to accurately identify and quantitate each compound using the modified method.

See Figures 1 and 2 for example chromatograms and spectra for samples analyzed by the modified method (scanning for ions, 15, 29, 44, 41 and 56) illustrating a sample with and without the presence of trans-2-butene, respectively.

In Figure 1, a prepared standard including the mixture of trans-2-butene and EtO at 0.25ppbv (individual concentration) was analyzed by SIM scanning for ions 15, 29, 44 as well as 41 and 56. At the target retention time window for EtO and trans-2-butene, the sample spectrum captured strong signals for ions 15, 29 and 44 as well as ions 41 and 56, which indicates and confirms the presence of trans-2-butene. In addition, the chromatograms for ions 41 and 56 were further examined to confirm that the first peak is correctly identified as trans-2-butene, and the second peak detected at 12.466 minutes is determined to be EtO and quantitated as such (determined concentration circled in figure as 0.24ppbv).

In Figure 2, an ambient sample collected at Willowbrook Village Hall on 19th November, 2018 was analyzed by SIM scanning for ions 15, 29, 44 as well as 41 and 56. At the target retention time window for EtO and trans-2-butene (established by standards), the sample spectrum captured strong signals for ions 15, 29 and 44 but minimal to no signal for ions 41 and 56, which indicates the absence of trans-2-butene. Also, by comparing to the EtO reference spectrum recorded from an EtO standard analyzed by the contract laboratory, the relative ratios of the sample for ions 15, 29 and 44 match closely with the established reference ratios. Coupled with the retention time

¹ https://www.epa.gov/sites/production/files/2015-07/documents/epa-to-15_0.pdf

window, the peak detected at 12.395 minutes is determined to be solely EtO and quantitated as such (determined concentration circled in figure as 3.38ppbv).

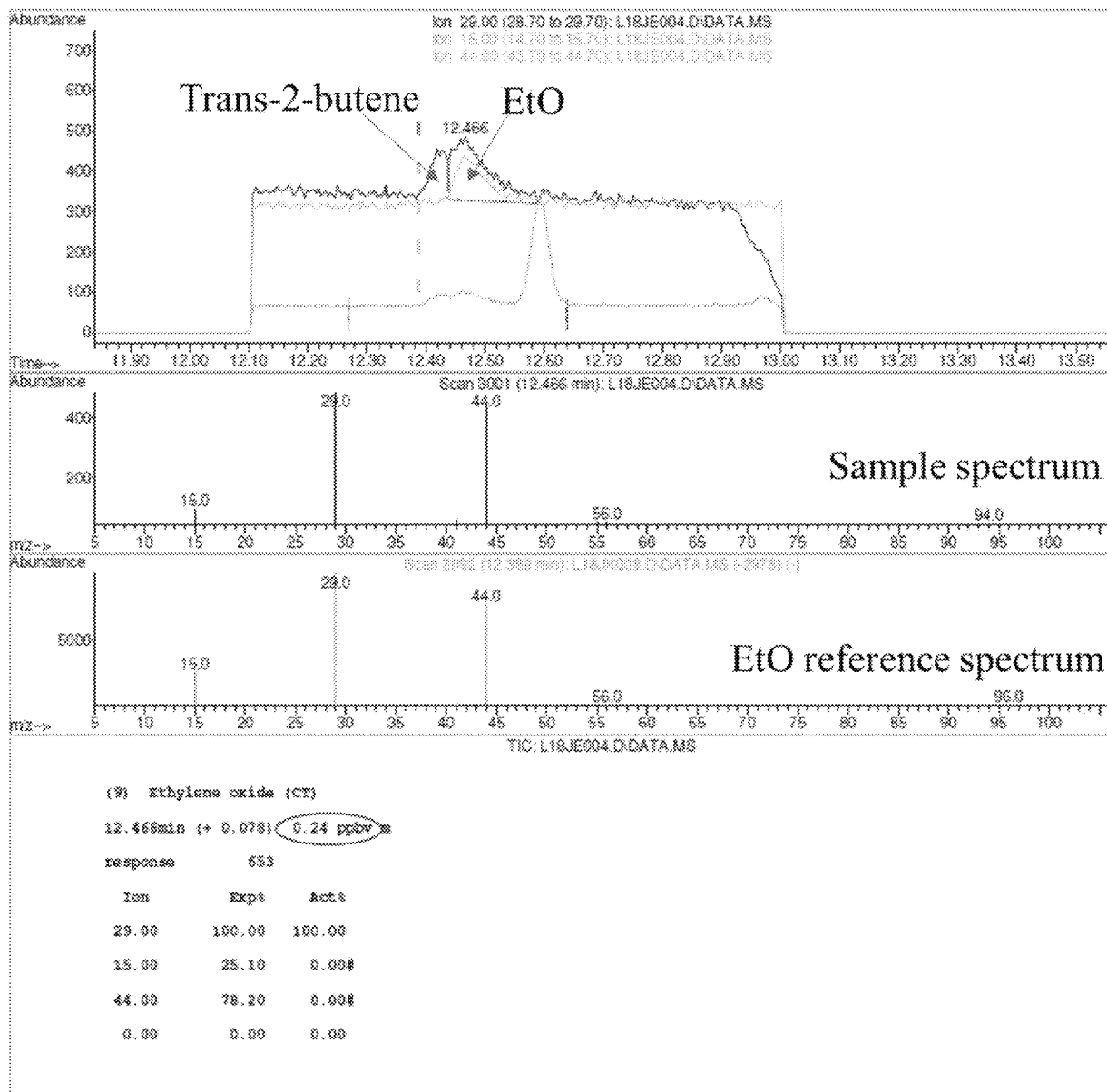


Figure 1. Example chromatogram and spectrum for a mixture standard (including both trans-2-butene and EtO) analyzed for EtO by the modified TO-15 method.

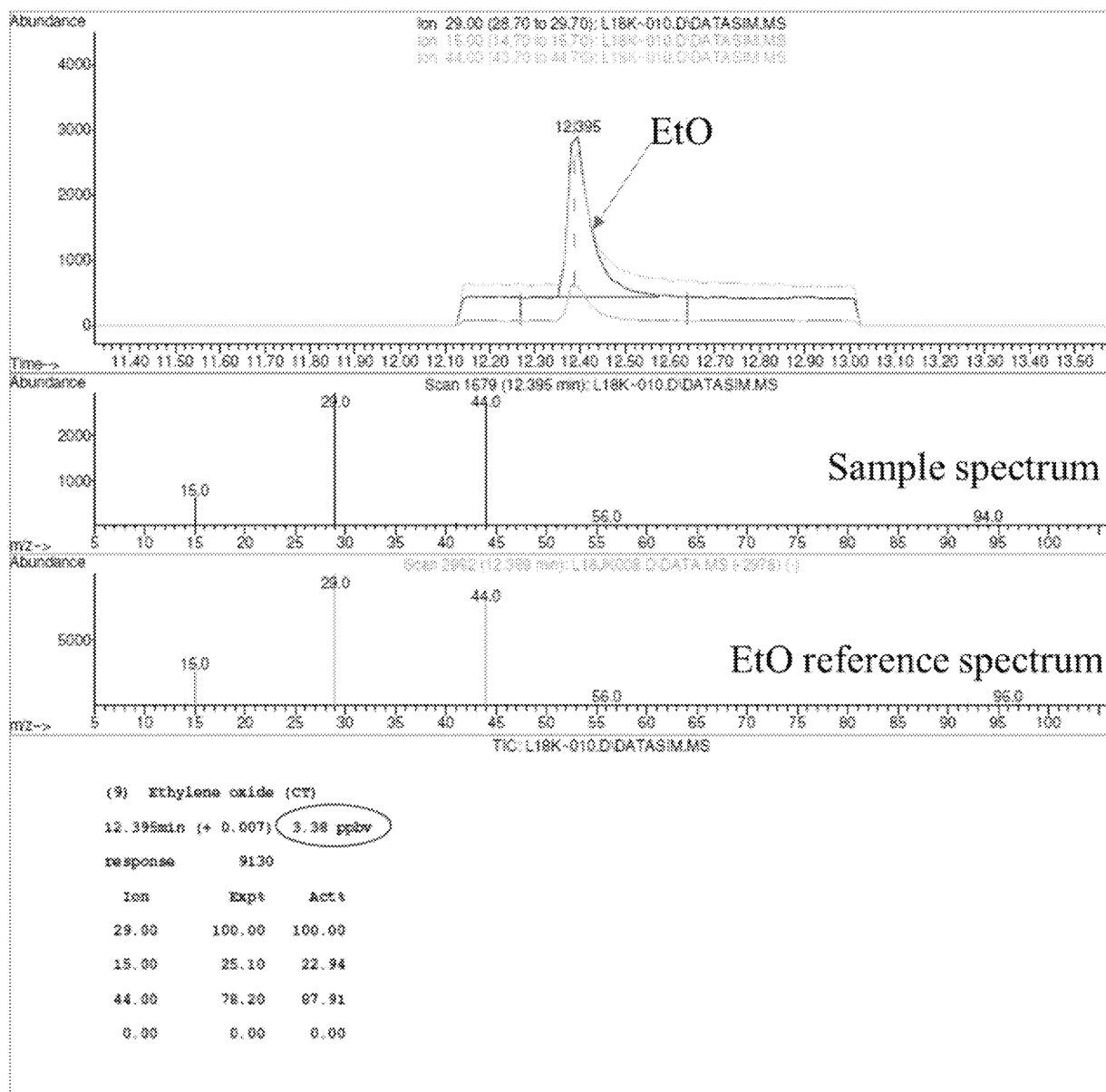


Figure 2. Example chromatogram and spectrum for a sample (collected at Willowbrook Village Hall on November 19th) analyzed for EtO by the modified TO-15 method.